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OSMOTIC PRESSURE, SEMIPERMEABLE MEMBRANES, AND THE BLISTERING OF PAINT[1]

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ABSTRACT

Although it has been known for several years that the blistering of paint on the outside of houses is caused by moisture, it has never been explained how the moisture gives rise to the large pressure required to separate a film of paint from wood. Recent experiments of Hopkins and Smart have shown that blistering occurs only when there is a temperature gradient. If the temperature of the paint film is below the condensation point so that the migrating moisture accumulates as liquid water in the pores of the wood, it is possible to suggest a mechanism, analogous to osmosis, which will give rise to large hydrostatic pressures. In the traditional osmotic experiment the role of hydrostatic pressure is to raise the vapor pressure of the solution until it is equal to that of the pure solvent and thereby to prevent any further movement of solvent molecules through the semipermeable membrane. In the blistering of paints, moisture accumulates as liquid water in the pores in the wood until the hydrostatic pressure exerted by the confining boundaries is great enough to raise the vapor pressure to the point where no further migration can take place. This hydrostatic pressure, if exerted against the paint film, is quite sufficient to account for blistering.

For several years it has been known that the blistering of paint on the outside of houses is associated with the presence of moisture in the underlying wood. Although the moisture is undoubtedly the cause of the blistering, no one has yet satisfactorily explained how it can give rise to the large force necessary to separate a well-bonded film of paint from wood. Measurements have shown that this force is seldom less than 200 pounds per square inch and it has been found to be as great as 500. No acceptable explanation has been put forward to account for forces of this magnitude; vapor pressures are obviously much too small and the pressures associated with temperature change can hardly apply.

It has been suggested by Dunn (2) that some type of osmotic phenomenon may be responsible. He suggests that the water in the system contains dissolved salts and the wood acts as a semipermeable membrane in such a way that typical osmotic pressures are built up. Although the pressures required are of the same order as those normally encountered in osmotic systems, this

explanation fails to carry conviction because it is not easy to see how the necessary juxtaposition of solution, membrane, and solvent can arise.

Recently, some experiments described by Hopkins and Smart (4) have introduced a new factor into the problem. Hopkins and Smart find that the presence of moisture in the wood is not in itself sufficient to cause blistering; the moisture must be combined with a temperature gradient. On the basis of this observation we suggest a mechanism which will lead to a transfer of moisture similar to osmosis and which will give rise to pressures of the same magnitude.

OSMOTIC PRESSURE

In the traditional picture of osmosis, a solution and pure solvent are separated by a membrane that can be penetrated by the molecules of the solvent but not by those of the solute. The molecules of the solvent diffuse through the membrane until the excess of hydrostatic pressure on the solution reaches a value π which is just sufficient to prevent any further transfer. The excess hydrostatic pressure π is a measure of the osmotic pressure of the solution.

Current ideas on diffusion through membranes allow us to present a simple explanation of osmosis. The action of the semipermeable membrane depends on the fact that the solvent molecules can interact with the membrane and are thus able to penetrate it whereas the solute molecules have no affinity for the membrane and are repelled. The interaction between solvent molecule and membrane may be described as either an adsorption or a solution depending on whether the movement of the molecules is considered to take place along internal surfaces or through the molecular arrangement of the solid itself. In either hypothesis the solvent molecules are adsorbed at one surface of the membrane, migrate through it by some sort of activated diffusion, and, on reaching the other surface, are desorbed into the solution. For osmosis, the actual mechanism of movement through the membrane is not important; we need only to assume that as long as there is a concentration gradient the migration of molecules will continue.

To understand osmosis it is necessary to study what takes place at the two surfaces. At one surface we have an adsorption of molecules from the solvent and at the other a desorption into the solution. From the kinetics of adsorption, we know that the molecules of the solvent will continue to be adsorbed as long as the vapor pressure (or the activity) of the solvent is greater than that of the adsorbed molecules on the membrane. Similarly at the surface in contact with the solution the molecules will desorb as long as the vapor pressure of the adsorbed molecules is greater than that of the solution. The transfer of solvent will stop only when the vapor pressure of solvent, of solution, and of adsorbed molecules is the same. In the traditional osmotic experiment, the balancing of vapor pressure arises through the effect of hydrostatic pressure on the solution; the hydrostatic pressure increases until it is just sufficient to raise the vapor pressure of the solution to the point where it is equal to that of the solvent. At that point there will be no further transfer of solvent and the system is in equilibrium.

On the basis of this picture it is simple to obtain an expression for the osmotic pressure. From thermodynamics we have the following expression for the effect of hydrostatic pressure on the vapor pressure of a liquid (3):

[1]
$$\frac{\partial p}{\partial P} = \frac{\bar{V}}{RT} p$$

where p is the vapor pressure, P the hydrostatic pressure, and $\bar{V}$ the molar volume of the solvent. If p_s is the vapor pressure of pure solvent and p the vapor pressure of solution under a hydrostatic pressure of one atmosphere, we have

$$\int_p^{p_s} \frac{\partial p}{p} = \frac{\bar{V}}{RT} \int_1^P dP,$$

$$\log \frac{p_s}{p} = \frac{\bar{V}}{RT} (P - 1).$$

Since the osmotic pressure is defined as the excess of the hydrostatic pressure on the solution over that on the pure solvent, we have for the osmotic pressure in atmospheres the expression

[2]
$$\pi = \frac{RT}{\bar{V}} \log \frac{p_s}{p}.$$

This expression agrees with that obtained by conventional methods.

THE BLISTERING OF PAINTS

In order to study the problem presented by the blistering of paint, let us consider a wooden panel painted on one surface and on the other exposed to water vapor at a vapor pressure p. Such an arrangement is representative of the experiments of Hopkins and Smart and is, in addition, an idealized presentation of conditions existing in the exterior walls of houses. We may consider the wooden panel to be a membrane permeable to water vapor and the paint film to be an impenetrable barrier. Water vapor will be adsorbed on the exposed surface and will migrate through the panel until it reaches the paint film. This migration will continue until the moisture distribution in the panel reaches such a value that the forces causing diffusion are everywhere balanced. The problem is to find out how, under such conditions, the moisture can exert a pressure great enough to separate the paint film from the wood and thus to form blisters.

If the temperature is constant throughout the system, it is obvious that when equilibrium is established the moisture content will be the same everywhere and will equal the equilibrium moisture content corresponding to the vapor pressure p. The vapor pressure immediately under the paint film must also be equal to p and consequently is much too small to have any effect on the adhesion of the paint. There is, under such conditions, no mechanism by which the moisture can exert a pressure of several hundred pounds per square

inch and we should not, therefore, expect blistering to occur. This, in fact, is what Hopkins and Smart have found; they say that "blistering does not occur unless there is a temperature difference." For the source of the pressure we must, therefore, look to the temperature difference, or, more specifically, since the moisture movement is always towards the cold side, to the fact that the paint film is colder than the exposed surface.

It is necessary to remember that in the traditional picture of osmosis the build-up of hydrostatic pressure occurs because there is a reservoir (the solution) capable of receiving the diffusing molecules in such a way that their accumulation does not directly affect the vapor pressure. Only when the accumulation of solvent is sufficient to change the hydrostatic pressure is the vapor pressure indirectly influenced. In the movement of moisture through the painted panel an analogous situation arises if the temperature of the paint film is low enough to condense the moisture. When condensation occurs the moisture accumulates as liquid water and the vapor pressure depends not on the quantity present but only on the temperature and pressure. As in the traditional picture of osmosis, the increase of vapor pressure necessary to stop the migration arises through the effect of hydrostatic pressure; the moisture continues to accumulate until the pressure exerted by the paint film is sufficient to raise the vapor pressure of the water to the point where there is equilibrium throughout the panel. In this way it is possible to obtain an effect completely equivalent to osmosis.

In order to obtain a quantitative estimate of the pressure let us examine in detail what happens under these conditions. On the exposed side assume that the temperature is T_i and the vapor pressure p; on the painted surface let the temperature be T_0 and assume that T_0 is below the dew point corresponding to conditions specified by temperature T_i and vapor pressure p. Under such conditions moisture is adsorbed at the exposed surface, migrates through the wood, and reaches the opposite surface where the movement is restricted by the paint film. The moisture content of the wood (i.e. the adsorbed moisture) will increase. Wood, however, is a porous substance and we must assume that, throughout the panel and especially beneath the paint film, there are pores capable of containing moisture in the form of vapor. As the moisture content of the wood increases the vapor pressure in these pores will also increase so as always to be in equilibrium with the adsorbed moisture. When, however, the vapor pressure reaches the saturation point it can increase no further and additional moisture will accumulate in the pores as liquid water. Until this point the migration of moisture has resulted in a steady build-up of the adsorbed moisture on the wood. With saturation a steady state is reached since the migration of moisture causes no further increase in either the adsorbed moisture or the vapor pressure in the pores and results only in the accumulation of liquid water. When the pores become filled, however, continued migration causes a build-up of hydrostatic pressure which ultimately will be transmitted to the paint film. We now proceed to calculate the magnitude of this pressure.

The thermodynamics is similar to that of the traditional osmotic experiment. As before the relation between hydrostatic pressure P and vapor pressure p is given by

$$\frac{\partial p}{\partial P} = \frac{\bar{V}}{RT} p.$$

Integrating we get

$$\int_{p_0}^{p} \log p = \frac{\bar{V}}{RT}(P - 1)$$

where p_0 is the saturation pressure corresponding to the temperature T_0. For the excess pressure π we obtain the expression

[3] $$\pi = \frac{RT}{\bar{V}} \log \frac{p}{p_0}.$$

In this derivation we assume that the diffusion process and the build-up of hydrostatic pressure will continue until the vapor pressure is everywhere equal to p, the pressure on the exposed side. Since there is a temperature gradient in the panel, this assumption would be true only if the vapor pressure were the operating force for diffusion. We have suggested recently (1) that the operating force for the diffusion of an adsorbed gas is the "spreading" (two-dimensional) pressure of the molecules adsorbed on the internal surfaces of the adsorbent. This "spreading" pressure, however, is a complex function depending on the adsorption isotherm and it would unnecessarily complicate our discussion if we were to attempt to make the derivation rigorous by the use of "spreading" pressures. Although, within the wood itself, diffusion will only cease when the "spreading" pressures are everywhere balanced, at the surfaces where adsorption and desorption take place the vapor pressures are the controlling factors; only when the vapor pressure of the liquid water in the pores is equal to that of the adsorbed moisture on the surface of the wood will desorption cease. Thus, although we introduce an error by the assumption that at equilibrium the vapor pressures will everywhere be equal to p, this error will be small and will in no way vitiate our conclusion.

To obtain numerical values for the pressure π we use the following values for the constants in equation [3]:

$R = 82.07$ (π is in atmospheres),

and $\bar{V} = 18$ cc.

We take T, which is equal to T_0, as 0°C.

Then $\pi = 2866 \log_{10}(p/p_0)$ atmospheres.

We shall assume that the relative humidity on the inside of the panel is 50% and thus that p is one half the saturation pressure at T_i. On this basis when T_i is greater than 10° C. condensation will occur beneath the paint film. Table I gives the hydrostatic pressures that would be built up before the migration of the moisture would stop.

It is apparent from Table I that immediately condensation occurs the hydrostatic pressure required to prevent the migration of moisture rises with

TABLE I

T_t(° C.)	P(mm. Hg)	p/p_0	$\log_{10}(p/p_0)$	π(atm.)
10	4.6	1.00	0.000	0.00
12	5.3	1.16	0.061	175
14	6.0	1.31	0.117	335
16	6.8	1.48	0.170	487
18	7.7	1.68	0.225	645
20	8.8	1.92	0.283	811

temperature difference very quickly to a high value. There is no difficulty in accounting for pressures which could easily displace any paint film. The assumption of 50% relative humidity is conservative since in walls where blistering occurs it is most likely that the humidity on the inside of the panel would be much higher than this and indeed might be close to saturation. With high humidities a small temperature difference would give rise to hydrostatic pressures of the magnitude required. One can conclude, therefore, that, when moisture moves through a wooden panel under the influence of a temperature gradient such that condensation occurs at the paint film, a hydrostatic pressure of considerable force will be built up and this pressure is quite sufficient to account for blistering of paint.

It should be emphasized that, for this discussion, conditions have been idealized; it is improbable that the movement of moisture through a panel in a building would occur in such a straightforward manner. The figures given in the table represent the pressure that would be exerted at equilibrium. This, of course, is seldom attained since the confining forces will probably break long before equilibrium and will allow the accumulation of moisture to proceed. The calculations are based on a temperature difference extending from one side of the panel to the other. Because of the complex structure of wood, it is not certain that all of this temperature difference is applicable. It may be that the temperature gradient through only a fraction of the thickness of the wood is operative and that in using the total temperature difference we have increased the effect unduly.

We should point out in addition that idealized conditions with a steady flow of moisture from the exposed surface to the paint film are not essential to the argument. If the temperature at the outer surface of a panel, originally at constant temperature and uniform moisture content, were suddenly to drop below the condensation point, moisture would migrate to the paint film, condense, and the pressure would build up as described above. To eliminate blistering on houses, therefore, it is not sufficient to prevent the movement of moisture from the interior but in addition the entry of moisture from the exterior through cracks and openings must be eliminated.

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INCREASING THE FOOD VALUE OF WHEY BY YEAST FERMENTATION

IV. FEEDING TRIALS WITH MICE[1]

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ABSTRACT

Nutritional studies with mice were conducted on powdered whey which had been fermented by *Torula cremoris*. Yeast-whey was shown to possess more protein, fat, thiamine, riboflavin, calcium, and phosphorus than skim milk. When it was used in conjunction with a wheat–oats ration, its protein supplementary value was equal to that of dried skim milk even though its methionine content was apparently lower. Yeast-whey ranked with dried brewers' yeast as a vitamin source, except in the case of thiamine.

INTRODUCTION

Previous work (4) at this institution has shown that it is feasible to produce a high protein – low lactose whey powder from cheese whey fermented by *Torula cremoris*. This work was successful in a pilot plant and could be adapted to large-scale operation.

Since the analysis of the powdered samples revealed a high protein content, it was thought that the product might be a valuable feed supplement. However, the suitability of a feed is not always evident from its gross chemical composition but may depend upon protein quality and the balance of other nutritive components. Therefore, it was decided to conduct a feeding trial with this powder before any definite recommendations were made.

Previous nutrition studies of food yeast (1) indicated that the unfavorable calcium: phosphorus ratio of this product was detrimental to good bone development in the young pig. Other reports (3, 6) showed that yeast protein could be substituted for vegetable protein in swine rations with no harmful effects. Similarly, studies with poultry (2, 5) indicated that yeast protein could be used to advantage. Dried whey has been chosen by other investigators (7, 8) because of unidentified factors contained therein. Lactose apparently was not essential in these rations and in some cases whey with a diminished lactose concentration was superior to the usual product (7).

EXPERIMENTAL METHODS

Several lots of fermented whey powder were prepared and analyzed according to the directions outlined in a previous paper (4). The analyses included tests for moisture, protein, solubility, ash, riboflavin, thiamine, phosphorus, and calcium. The whey powder was then variously incorporated into diets as either vitamin or protein supplements for feeding studies.

Experiment 1

The design of this study was a $2 \times 3 \times 4$ factorial involving two basal diets (grain and 'synthetic') containing 13% crude protein, three B-vitamin treatments (nil, 2% dried brewers' yeast, and 2% yeast-whey), and four protein supplements (yeast-whey, yeast-whey + methionine, dried skim milk, and soybean-oil meal + fish meal + alfalfa meal) to increase the protein level of the complete rations to 18%.

The formulation of the grain basal ration was as follows: wheat 66.0, oats 30.5, minerals 3.5*; and of the 'synthetic' ration: corn starch 70, sucrose 3, minerals 4, cellulose (solka floc BW40) 7, vitamin-free casein 13, crisco 3, and monosodium glutamate 0.25. Vitamins A and D were added following the incorporation of the B-vitamin and protein ingredients.

The various protein supplements were chosen to show the value of adding methionine to yeast-whey, since this amino acid is a major limiting factor in whey protein, and to compare these yeast-whey preparations with products which ordinarily produce good growth when used in conjunction with cereal grain rations. The fourth protein supplement employed soybean-oil meal, fish meal, and alfalfa meal in the ratio 3:3:1.

Each of the rations was fed individually in four replicates to weanling mice of Carworth No. 1 strain, weighing initially 8.0 to 9.0 gm. and of age 18 to 23 days. The mice were housed at 28°C. in battery cages containing wire mesh floors. Food and water were provided *ad libitum* and accurate feed records were kept. The assay period was 14 days.

Experiment 2

This study was designed to provide further information with regard to the adequacy of thiamine and pantothenic acid in yeast-whey. For this purpose the 'synthetic' basal ration was supplemented with soybean-oil meal + fish meal + alfalfa meal as before and yeast-whey as 2% of the diet. To this basal diet were added (*a*) no supplement, (*b*) thiamine at 0.5 mgm./lb. of diet, (*c*) pantothenic acid at 5 mgm./lb. of diet, (*d*) thiamine and pantothenic acid, (*e*) thiamine, pantothenic acid, and 2% brewers' dried yeast.

Feeding, management, and recording of data were carried out as in Experiment 1.

RESULTS AND DISCUSSION

A detailed analysis of the fermented whey powder is given in Table I. Also included for purposes of comparison are values for dried skim milk, dried whey, and brewers' dried yeast.

The results of the growth trials were found to have been independent of variations in initial weights of the mice but were affected by differences in feed consumption ($r = 0.67$, highly significant). Examination of the gains adjusted for feed intakes revealed that, aside from the two basal diets, the differences in gains were not due to differences in palatability of the rations offered. Be-

*Mineral Supplement: bone meal 140, ground limestone 235, NaCl 125, FeSO$_4$ 10, MgSO$_4$ 10, MnSO$_4$ 0.25, CuSO$_4$ 0.25, and KI 0.25 gm.

TABLE I

CHEMICAL ANALYSES OF YEAST-WHEY POWDER, SKIM MILK POWDER, WHEY POWDER, AND
BREWERS' DRIED YEAST

Feedstuff	Water (%)	Protein (%)	Fat (%)	Ca (%)	P (%)	B_1 (mgm./lb.)	B_2 (mgm./lb.)
Yeast-whey	5.3	38.5	12.1	2.5	2.2	3.6	21.3
Skim milk powder[1]	5.8	34.7	1.2	1.3	1.0	1.6	9.5
Whey powder[1]	6.5	12.2	0.8	0.9	0.7	1.8	13.0
Brewers' dried yeast[1]	6.2	49.3	1.0	0.1	1.6	35.0	18.6

[1]*Data from "Feeds and feeding", F. B. Morrison, Morrison Publishing Co.*

cause of the evident influence of the basal diets upon the responses to vitamin
and protein supplements the value of yeast-whey can best be studied by con-
sidering the 'adjusted gains' for the two basal diets separately.

In Table II it is evident that, when used as a supplement to grain rations,
yeast-whey performs as well as high quality protein supplements of animal or
animal–vegetable origin. Addition of methionine was of no value, thus it would
appear that yeast-whey was satisfactory in both protein quantity and quality
for use in practical diets. B-vitamins also appeared to be adequate in all
instances.

In a more critical test of protein quality and B-vitamin adequacy, with the
'synthetic' basal, quite pronounced differences occurred. The growth obtained
on this basal diet with yeast-whey as a protein supplement was significantly less
than that with skim milk powder, and since the further addition of methionine
resulted in normal growth, it is evident that the methionine content of yeast-

TABLE II

FOURTEEN-DAY WEIGHT GAINS OF MICE FED YEAST-WHEY AS A PROTEIN SUPPLEMENT OR A
VITAMIN SUPPLEMENT TO GRAIN OR 'SYNTHETIC' RATIONS

(Gains adjusted for differences in feed intakes)

Protein supplement	Vitamin supplement (gm.)		
	Nil	Brewers' dried yeast	Yeast-whey (gm.)
Grain basal			
Yeast-whey	10.8[1]	10.1	10.4
Yeast-whey + methionine	10.7	11.6	11.8
Skim milk powder	10.7	10.9	11.5
Soy–fish–alfalfa[2]	10.3	10.4	10.8
'Synthetic' basal			
Yeast-whey	9.8	10.4	10.4
Yeast-whey + methionine	11.5	11.2	10.6
Skim milk powder	11.3	11.1	11.4
Soy–fish–alfalfa[2]	7.7	12.5	7.8

[1]*Necessary difference = 1.7 gm., P = 0.05.*
[2]*Soybean-oil meal, fish meal, and alfalfa meal.*

whey was a limiting factor in this study. It appears that B-vitamins were not deficient when yeast-whey was used as the protein supplement.

The mixture of soybean-oil meal, fish meal, and alfalfa meal undoubtedly provided a protein supplement of high biological value but it resulted in poor gains when used as the only addition to the 'synthetic' basal diet. Excellent responses were obtained when 2% brewers' dried yeast was added whereas a similar quantity of yeast-whey failed to effect any improvement, thus indicating that a B-vitamin deficiency was involved and that yeast-whey had a low content of the factor(s) concerned. From Table I data it seems improbable that yeast-whey was deficient in riboflavin. The estimated niacin content of the soybean-oil meal + fish meal + alfalfa diet exceeded that of the skim milk diets, thus ruling out this vitamin. Distinct possibilities existed however that thiamine, pantothenic acid, and possibly other vitamins were involved.

TABLE III

THE EFFECT ON GROWTH RATES OF ADDING THIAMINE, PANTOTHENIC ACID, AND/OR BREWERS' DRIED YEAST TO YEAST-WHEY AS A VITAMIN SUPPLEMENT IN MOUSE DIETS

Addition to yeast-whey	Gain (gm.)	Feed consumed in gm. per gram gain
Nil	6.4	5.7
Thiamine	13.6	3.2
Pantothenic acid	8.3	4.3
Thiamine + pantothenic acid	13.5	3.8
Thiamine + pantothenic acid + brewers' yeast	14.6	3.5

The results of Experiment 2 confirmed the ineffectiveness of yeast-whey as a vitamin supplement to the soy–fish ration. The addition of thiamine permitted normal growth but the further addition of pantothenic acid was of no value. It therefore is probable that yeast-whey used as a vitamin supplement differs appreciably from brewers' dried yeast only in thiamine content.

Despite the fact that yeast-whey has been shown to possess certain limitations it is important to recognize its merits. It has been possible to increase the protein content of whey powder threefold by fermenting out the lactose with *Torula cremoris* (4), and therefrom to obtain a protein supplement of high biological value for use in practical rations. Its thiamine and riboflavin values considerably exceed those of skim milk powder, and although its thiamine content falls below that of brewers' dried yeast, this may not be too serious a limitation, however, since it is riboflavin, not thiamine, that is more often deficient in grain rations commonly fed to livestock.

SUMMARY AND CONCLUSIONS

The nutritional value of yeast-whey as a protein and vitamin supplement was investigated by chemical analyses and feeding trials with mice. It was shown that:

1. Yeast-whey contained more protein, fat, thiamine, riboflavin, calcium, and phosphorus than skim milk powder.

2. Its protein supplementary value was equal to that of skim milk powder as an addition to a wheat–oats ration, but was somewhat deficient in methionine according to tests with semipurified diets.

3. As a vitamin B-complex supplement yeast-whey compared favorably with brewers' dried yeast except in the case of thiamine.

ACKNOWLEDGMENT

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STUDIES ON IMPROVING THE EASE OF RECONSTITUTION
OF SKIM MILK POWDER[1]

By D. L. Gibson[2] and J. W. Raithby[3]

ABSTRACT

In an effort to improve the ease of reconstitution of skim milk powder, methods of reconstitution and techniques of manufacture were studied. It was found that reconstitution at a temperature of approximately 50° C. gave the highest wettable value. Reconstituting above 60° C. markedly reduced reconstitutability. Powder particles with a diameter of less than 15 microns were more difficult to reconstitute than those having a diameter of 15 to 25 microns. The addition of up to 25% by weight of sugars or sugar derivatives produced no appreciable effect on wettability unless they were added after drying. Surface active agents of the Tween variety at concentrations as low as 0.1% by weight of the skim milk powder improved wettability.

INTRODUCTION

Hunziker (5) stated that a soluble milk powder when mixed with water in proportions approximately equal to those of normal fluid milk is capable of returning to a solution, suspension, and emulsion that will simulate the physical characteristics of normal milk. According to this definition, therefore, milk powder solubility means principally protein suspension stability, rather than true molecular solubility. The U.S. Quartermaster Corps (7) considered a powder to have good dispersability if it could produce a milk which, when swirled two or three times in a glass of water, resembled a glass of fresh milk. Thus it is apparent that the dispersability of a powder refers to the speed with which it becomes miscible with water.

It has been reported by Whittier and Webb (8) that dried, sweetened condensed milk is more easily reconstituted than normal dried milk. However, no experimental data have been found which would suggest the optimum quantity of sucrose that should be added to facilitate ease of reconstitution. Furthermore, there is some controversy concerning methods of reconstitution, especially with respect to temperature, which varies from 5° C. to 43° C. It is agreed by some workers (6, 9) that the reconstituted milk should be clarified and homogenized prior to pasteurization. The use of surface active agents as a means of improving the dispersability of whole milk powder has been investigated by Hollender (4). He felt that a combination of compounds giving a good hydrophilic–lipophilic balance was more effective than one compound alone in promoting dispersability of whole milk powder, though certain additives lost their effectiveness during storage more readily than others.

MATERIALS AND METHODS

1. *Drying Procedures*

Skim milk was preheated to 71° C. (160° F.) for five minutes prior to entering a 16 in. Mojonnier vacuum pan operating at 23 in. of vacuum at 55° C. (130° F.). The skim milk was condensed at approximately 35% solids, and cooled to 1.6° C. (35° F.). A spray drier similar to that described by Coulter (3) was employed, using an incoming temperature of 160° C. (320° F.) and an outgoing temperature of 71° C. The concentrated milk was heated to 43° C. (110° F.) and atomized by an air spray nozzle operating under 20 p.s.i.

2. *Standardization of Testing Techniques*

The test used for determining wettability was essentially the same as that described by Ashworth (2). Further tests included moisture analysis by the toluene distillation method and solubility index measured according to the American Dry Milk Institute methods (1).

3. *Studies on Reconstitutability*

1. A study was made on the effect of reconstitution temperature on wettability. In this trial two powders were used: (1) Powder A, commercially prepared sample; (2) Powder B, a sample from experimental drier. The powder was suspended in water at temperatures ranging from 10° C. to 80° C. Tests for wettability were conducted on each sample.

2. Samples from each lot were subjected to microscopical examination to determine the size of the milk particles.

3. The effect of sucrose, dextrose, sorbitol, and mannitol on the wettability of skim milk powder was investigated. They were added to the fluid concentrate to represent 0, 5, 10, 15, 20, and 25% of the total solids, after which the material was dried. In other experiments, the sugars and sugar derivatives were added to 100 gm. aliquots of a commercially prepared skim milk powder in amounts which would give 0, 5, 10, 15, 20, and 25% in the powder. In certain instances it was necessary to pulverize these additives to permit passage through a 40 mesh screen.

4. Several surface active compounds were studied to note their effectiveness in improving the wettability of skim milk powder. The surface active agents used were Span 20 (sorbitan monolaurate), Tween 20 (polyoxyethylene sorbitan monolaurate), Tween 21, and a 50:50 mixture of Span 20 and Tween 20. Stock solutions of these additives were prepared and added to condensed milk of known solids content to produce 0.5 and 1.0% of the agents in the powdered product.

Additional studies on Tween 20 were conducted and aliquots measured into a weighed sample of condensed skim milk of known solids concentration. The aliquots contained Tween 20 at concentrations which represented 0.01, 0.05, 0.1, 0.25, and 0.5% of the weight of skim milk powder. Wettability determinations were made on the powders obtained from the treated samples.

EXPERIMENTAL RESULTS

1. *Effect of Temperature of Reconstitution*

It was noted that the temperature of reconstitution had a marked effect on the wettability of skim milk powders (Fig. 1). Wettability increased with temperatures up to 50° C., at which point the wettability of the powders
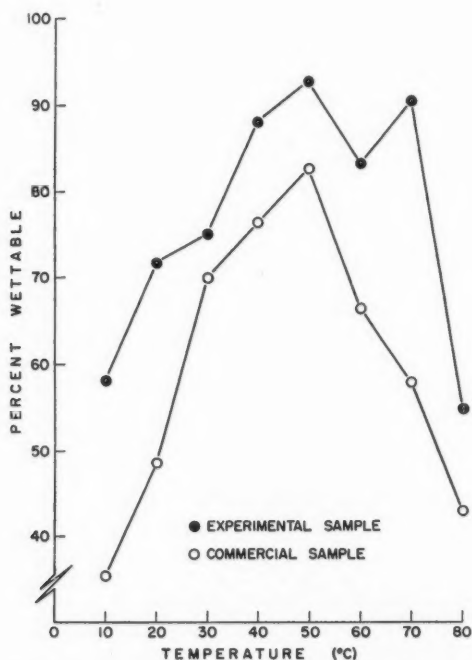

FIG. 1.   The effect of temperature of reconstitution on the wettability of skim milk powder.

examined appeared to be at a maximum. At 60° C. a decrease in wettability was observed which may be due, in part, to some protein denaturation. It was noted, however, that at 70° C. there was an increase in the wettability of the commercial sample but not of the experimental sample. Milks reconstituted at this temperature had a flaky appearance probably caused by protein denaturation. There was a marked decrease in wettability of both powders when reconstituted at temperatures above 70° C.

Although every precaution was taken to ensure a powder of uniform density and size, it was found that there was considerable variation in the diameter of particles in successive trials as indicated in Table I. It would appear that particle size influences the wettability of milk powder.

TABLE I

THE EFFECT OF PARTICLE SIZE ON THE WETTABILITY
OF SPRAY DRIED SKIM MILK POWDER

Diameter in microns most frequently observed	Range	Per cent wettable
10	5–25	48
10	5–20	50
14	8–16	65
12	5–20	63
16	10–30	98

2. *Effect of Sugar Addition*

The addition of sorbitol, mannitol, sucrose, and dextrose to the concentrate before drying had little or no effect on the wettability of the skim milk powder as noted in Fig. 2. Variations were observed between the various lots of powder.
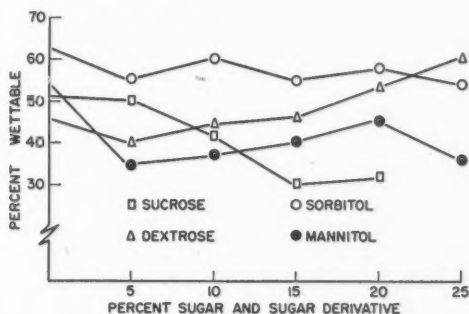

FIG. 2. The effect of sugar and sugar derivatives added before drying on the wettability of skim milk powder.
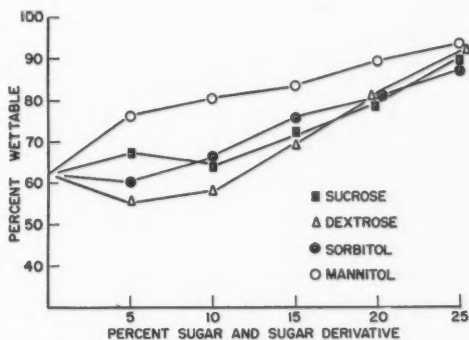

FIG. 3. The effect of sugar and sugar derivatives added to powder on the wettability of skim milk powder.

It is not likely, however, that the variations were due to the additives but rather to inherent differences in particle size of the different samples of powder.

When the sugars and sugar derivatives were added to the powder itself (Fig. 3), the wettability was improved with increased concentrations of the additives above 10%. The addition of 5% sugar and sugar derivatives had no significant effect on the wettability of the powder, whereas concentrations ranging from 15–25% were quite effective. There was no observable difference among the products tested with respect to their effect on reconstitution.

3. *The Effect of Wetting Agents*

In this study, Span 20, Tween 20, Tween 21, and a 50:50 mixture of Span 20 and Tween 20 were added to the condensed milk in an attempt to improve the wettability of the powder. The data from these studies are presented in Fig. 4 and indicate that some of these additives have a pronounced effect on the ease of reconstitution. The addition of Span 20 at the concentrations used
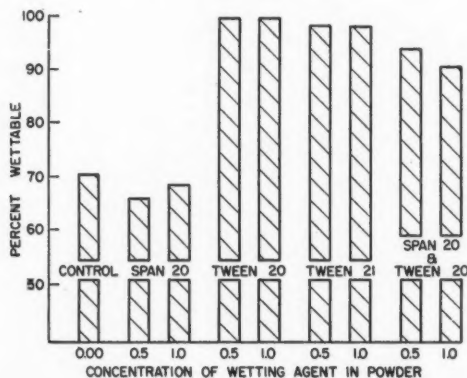

FIG. 4.   The effect of various surface active agents on the wettability of skim milk powder.

did not appreciably affect the wettability. This may be due to the fact that Span has a strong lipophilic attraction and consequently a lowered affinity for water. Both Tween 20 and Tween 21 had a marked effect on the wettability of skim milk powder when added at a rate of 0.5% by weight of the powder. Increasing the concentration of these two surface-active agents to ·1.0% of the powder produced no improvement in wettability. The combination of Span 20 and Tween 20 also improved the wettability of skim milk powder but not to the extent of Tween 20 when used alone. This slight reduction in wettability may be due to the lower concentration of Tween 20 for it was noted that the Span 20 had little or no effect on the wettability of skim milk powder.

It has been shown that both Tween 20 and Tween 21 markedly improved the wettability when used in concentrations as low as 0.5%. A study was made on the possibility of reducing this level even further and still retaining the

ease of reconstitution. The data presented in Fig. 5 indicate that there is a close relationship between the concentration of wetting agent and the per cent wettable value of the powder. The addition of Tween 20 at a concentration of 0.01% of the powder was observed to be slightly effective, whereas there was a marked increase in the wettability of the powder when the concentration was increased to 0.05%, reaching a maximum improvement at the 0.1% level. The data (Fig. 5) represent duplicate trials on the same lots of powder; one half was tested immediately after manufacture and the other after two weeks at room temperature. Although insufficient data are available to warrant definite conclusions, there were indications that Tween 20 lost some of its effectiveness during storage.
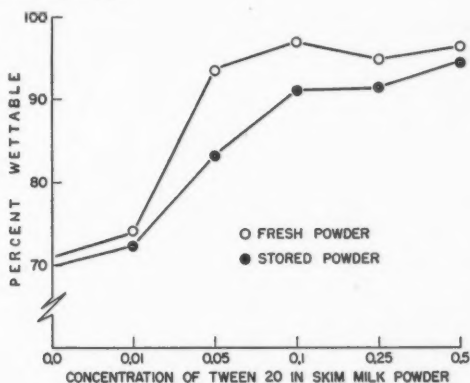

FIG. 5. The effect of varying amounts of Tween 20 added before drying on the wettability of skim milk powder.

DISCUSSION

One aspect of this investigation dealt with the optimum temperature for reconstituting skim milk powder. Since 50% of the powder is composed of lactose which forms a true solution in water, it is logical to assume that the powder will in some fashion behave like lactose. Since the rate at which lactose molecules dissolve is accelerated by heat, it is reasonable to expect that the dispersion of skim milk powder will tend to proceed similarly. However, the rate of dispersion of milk proteins may be accelerated by increases in temperature only to the point at which protein denaturation occurs. Accompanying denaturation of the milk proteins the solubility and ease of dispersion of the powder is lowered. Increasing the temperature up to 50–60° C. accelerates the dispersion of the powder because of its greater solubilizing effect on lactose and other milk constituents, whereas above this temperature loss of wettability results owing to protein denaturation.

A study on the influence of various additives affecting the ease of reconstitution of skim milk powder was undertaken. In connection with the addition of sugars and sugar derivatives it was thought that the incorporation of very soluble particles into the mass of powder might aid in its reconstitution

because these materials, being readily dissolved, would increase the area of contact between the powder particles and the dispersing medium. When these products were added to the powder itself, a marked increase in reconstitutability was noted. Little or no increase in reconstitutability was evident when sugars or sugar derivatives were added to the concentrate before drying. This was probably due to the fact that there were either particles of sugars or sugar derivatives present which were too small to act as foci for water penetration, or the sugar and sugar derivatives were masked within the powder particles and thus were making less contact with the water.

Reconstitutability increases at a rate corresponding to the concentration of sugar and sugar derivatives added to the powder. This increase may be due either to the numerical increase in readily soluble foci or to the lowered percentage of skim milk powder in the sample due to the presence of added soluble ingredients.

The other additives used to improve wettability were various surface active agents. These compounds may exert their effect by lowering the surface tension of the dispersing medium and thus allowing for the penetration of water into the interparticle spaces of the powder mass, or by orientating themselves into a layer on the particle surface and thus attracting the water into the powder mass. The different abilities to promote wetting exhibited by various surface active agents may be due to their varying affinities for water.

Although the Tweens (and possibly other surface active agents not included in this study) will improve the ease of reconstitution of skim milk powder, their incorporation into milk powder must await toxicological investigation.

SUMMARY AND CONCLUSIONS

1. The wettability of milk powder was enhanced as the reconstitution temperature was increased from 10° to 50° C. Above this temperature the powder became more difficult to reconstitute.

2. In an attempt to improve the ease of reconstitution, certain substances were added to the milk concentrate before and after drying. Sucrose, dextrose, sorbitol, and mannitol increased wettability when they were added to the powder. Little or no improvement was noted when sugars or sugar derivatives were added to the concentrated skim milk before drying.

3. The surface active agents Tween 20 (polyoxyethylene sorbitan monolaurate HLB 16.7) and Tween 21 (polyoxyethylene sorbitan monolaurate HLB 13.3) when added to the concentrate before drying in amounts up to 1% of the dry weight of the nonfat dry milk solids increased wettability. Span 20 (sorbitan monolaurate HLB 8.6), however, did not appreciably affect wettability.

ACKNOWLEDGMENTS

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NOTE

A SIMPLE DEVICE TO EFFECT CONTROLLED PORTIONWISE ADDITION OF SOLID REACTANTS TO REACTION MIXTURES UNDER ANHYDROUS CONDITIONS*

By R. A. B. Bannard

During certain chlorination studies it became necessary to add phosphorus pentachloride under anhydrous conditions to a system which was initially very sensitive to the action of this chlorinating agent. Since apparently no apparatus is commercially available to accomplish such an operation, the device shown in the diagram below was constructed and found to give the desired control over addition rate and freedom from contamination with moisture.
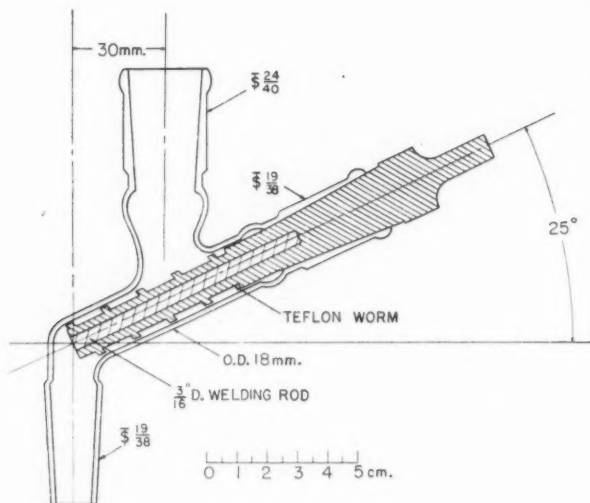

Fig. 1.

The addition tube was simply constructed from S.T. ground joints and "Pyrex" tubing of the sizes specified. The teflon worm was machined from 13/16 in. diam. teflon rod after a 3/16 in. diam. welding rod had been inserted as shown in the diagram to produce the necessary rigidity in the lathe. A worm pitch of two threads per inch was found to be most suitable to effect delivery of the powder without jamming or binding when a clearance of 0.5 mm. was allowed between the threads and the tube wall. A shoulder was left above the worm to prevent the powder from backing up the tube. The

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upper portion of the teflon adapter was machined to fit a S.T. 19/38 ground joint. The distance of travel of the powder in the tube should exceed one and one-half turns of the worm to prevent the powder from running. Teflon was chosen for construction of the worm since it is chemically inert, readily machined, and effects a tight seal in S.T. ground joints without requiring a lubricant.

In operation, the powder was weighed in a dry-box into an erlenmeyer flask with S.T. 24/40 ground joint which was then attached to the inverted addition tube. The addition assembly was then rapidly attached to the reaction flask and the powder transferred by manual operation of the worm. Prior calibration of the addition assembly establishes both the holdup of the system and the weight of powder delivered per turn. In the case of finely ground phosphorus pentachloride the holdup was 0.4–0.7 gm. and the delivery 0.67–0.70 gm. per turn. Precise control over the quantity of powder added during any time interval may thus be readily effected.

ACKNOWLEDGMENT

The assistance of Mr. R. MacLean of D.R.C.L. Experimental Machine Shop who fabricated the teflon worm is gratefully acknowledged.

NOTE ADDED IN PROOF. *A similar apparatus of all-glass construction has been reported by Swift, E. and Billman, J. H. Ind. Eng. Chem. Anal. Ed. 17: 600. 1945.*
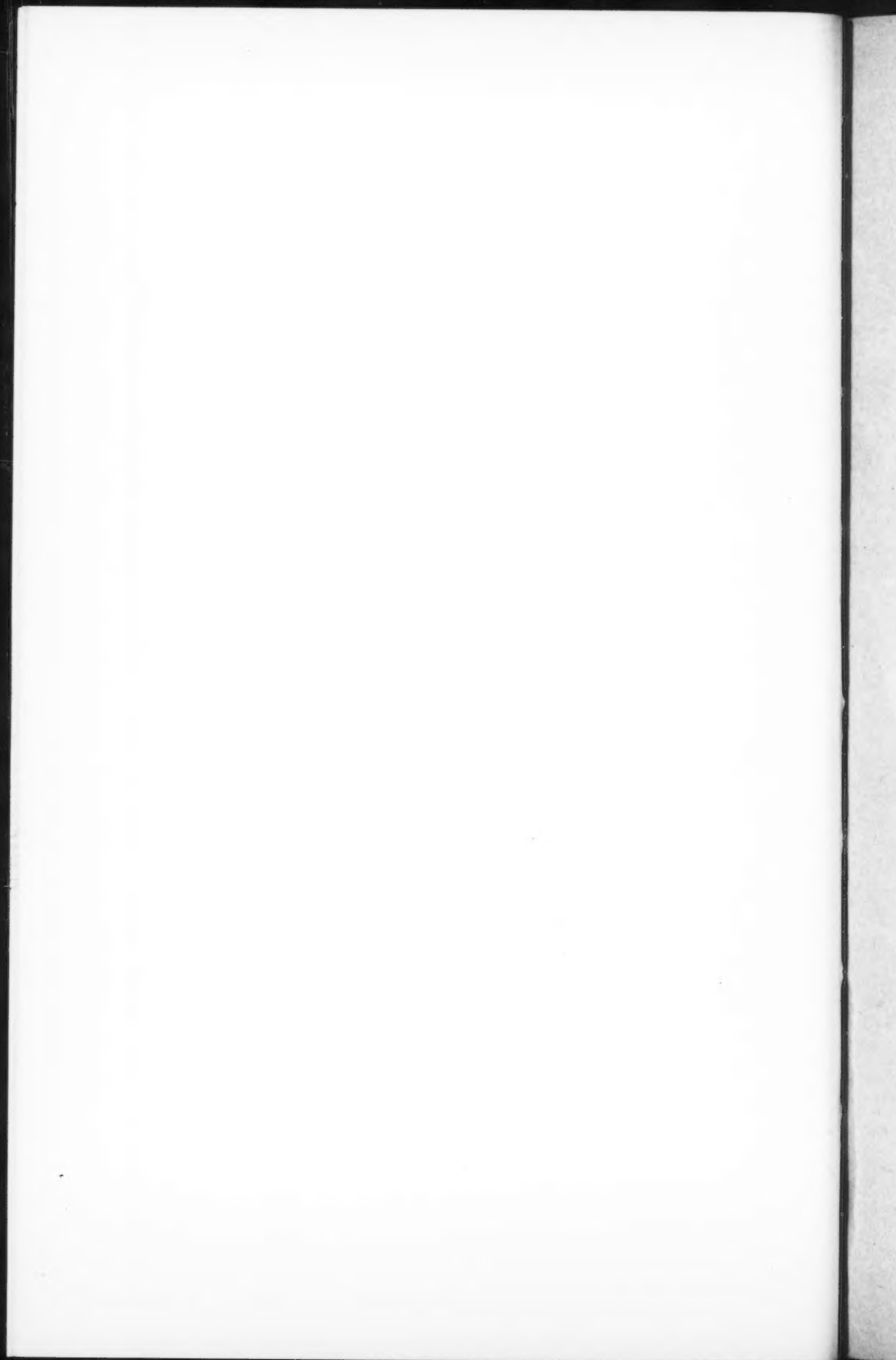
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